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AN INFRARED STUDY OF THE OXIDATION OF CARBON MONOXIDE
OVER SUPPORTED RHODIUM CATALYSTS(U) AUBURN UNIV AL DEPT
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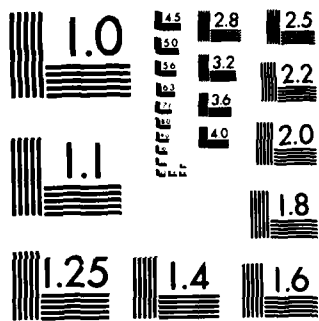
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<p>The reaction of carbon monoxide and oxygen over supported rhodium films has been studied using infrared spectroscopy. The focus of the work was the reactivity of the various CO/Rh/X (X=Al₂O₃, SiO₂, TiO₂) surface states for supported catalysts having high and low Rh loading. Under the reaction conditions the "linear CO" species was the most stable toward oxidation, but this could have been a result of an oxidized Rh surface. A new CO/Rh surface species has been proposed which exhibits an infrared band at 2000/cm⁻¹ for a 0.5% Rh/TiO₂ film. This species is believed to be a bridged carbonyl between Rh⁴¹ and the TiO₂ support.</p> <p><i>Handwritten:</i> Infrared, CO, Rh, TiO₂, and Carbon dioxide.</p>			
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Carbon Monoxide over Supported Rhodium Catalysts**

by

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AN INFRARED STUDY OF THE OXIDATION OF CARBON MONOXIDE OVER SUPPORTED
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Abstract

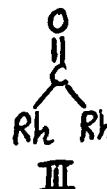
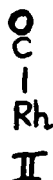
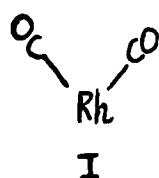
The reaction of carbon monoxide and oxygen over supported rhodium films has been studied using infrared spectroscopy. The focus of the work was the reactivity of the various CO/Rh/X (X=Al₂O₃, SiO₂, TiO₂) surface states for supported catalysts having high and low Rh loading. Under the reaction conditions the "linear CO" species was the most stable toward oxidation, but this could have been a result of an oxidized Rh surface. A new CO/Rh surface species has been proposed which exhibits an infrared band at 2000 cm⁻¹ for a 0.5% Rh/TiO₂ film. This species is believed to be a bridged carbonyl between Rh⁺¹ and the TiO₂ support.



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1. Introduction

Although numerous studies of the catalytic hydrogenation of CO over supported Rh catalysts have been reported [1], the oxidation reaction for CO over these catalysts has received considerably less attention. It is well established that the oxidation of CO over Rh at moderate temperatures generally follows a Langmuir-Hinshelwood mechanism having negative order in carbon monoxide and positive order in oxygen with the reaction of $\text{CO(a)} + \text{O(a)}$ being the rate determining step [2-8]. The oxidation reaction over supported Rh is particularly adapted for infrared study because CO adsorbs on supported Rh in several well-characterized states as shown below [9-12]. Species I, the "gem dicarbonyl" species, is characterized by two



sharp infrared bands near 2030 and 2100 cm^{-1} which do not shift significantly in frequency with coverage and hence have been attributed to the symmetric and antisymmetric stretching modes of CO bonded to isolated Rh sites [9-12], although this issue concerning the dispersion of the Rh remains controversial [13-15]. Also, the Rh in species I is almost certainly in the $+1$ oxidation state [10-12,16,17]. Generally catalysts prepared with low Rh loading (0.5% Rh/support) contain only this surface species. If the species I sites were not isolated a shift in frequency with coverage of the two vibrational bands would be expected due to dipole-dipole interaction [18], local field effects [19,20], vibrational coupling [20], or changes in metal-carbon backbonding due to the change in

CO coverage [21]. However, electron-microscopy experiments for similar supported Rh catalysts containing low loading (1% Rh/Al₂O₃) have indicated that species I sites are composed of "rafts" containing at least eight Rh atoms [13], and recent EXAFS data [14,15] have shown that 0.5% Rh/Al₂O₃ catalysts do contain some clusters with the adsorption of CO possibly causing disruption of the clusters [15]. Species II, the "linear CO" species, and species III, the "bridged carbonyl" species, exhibit infrared bands in the 2040-2080 cm⁻¹ and 1850-1950 cm⁻¹ regions, respectively, which do shift to higher frequency as coverage increases and must correspond to Rh metal cluster sites. The order of reactivity of these states with oxygen to produce carbon dioxide has been of interest in these laboratories as well as elsewhere [22,23]. This paper will report some of our recent findings in this regard as well as a new surface species for CO/Rh/TiO₂.

2. Experimental

The supported Rh catalysts used in this study were prepared as 0.5% or 10.0% by weight Rh/X (X=Al₂O₃, TiO₂, SiO₂) films by spraying a slurry of appropriate amounts of RhCl₃·3H₂O, support material, nine parts spectroscopic grade acetone, and one part water onto a heated 25 mm CaF₂ infrared window using a specially designed atomizer. Evaporation of the solvents left a uniform film of RhCl₃·3H₂O/X on the window which was then positioned in a Pyrex infrared cell/reactor of the type designed and used here previously [1,10-12]. Following evacuation to ca. 3x10⁻⁶ Torr, the samples were heated under vacuum at 430 K for 2 hr. Then three reduction cycles (Matheson Research Grade Hydrogen) at 75 Torr for periods of 20,

10, and 5 min were performed, with evacuation between each cycle. The samples were heated for an additional hour at 440 K under vacuum and then cooled to ambient temperature and evacuated until the base pressure was at least 3×10^{-6} Torr. At this time mixtures of 2 parts CO, 1 part O₂ generally at a total pressure of ca. 21 Torr were introduced into the cell, and the infrared spectra were recorded as a function of temperature.

The RhCl₃·3H₂O employed was obtained from Alfa Products, Inc. and used without further purification. The support materials used were alumina (Degussa Aluminum Oxide C, 100 m²g⁻¹), titania (Degussa Titanium Oxide P25, 50 m²g⁻¹), and silica (Cabot Cab-O-Sil M-5, 200 m²g⁻¹). The degrees of Rh dispersion for the various supported Rh catalyst films were not determined. All gases were of the highest purity obtainable from Matheson. The infrared spectra were generated by a Perkin-Elmer 983 spectrometer which was interfaced to a Perkin-Elmer data station. The data station was used for storage and manipulation of the spectra, particularly for difference spectra. The spectrometer was operated at a resolution of 5 cm⁻¹ in the 3000-1200 cm⁻¹ region. A quantitative determination of the yield of CO₂ was not made in this study.

3. Results and Discussion

The behavior of the adsorbed CO species infrared bands under oxidation reaction conditions must be highly dependent upon the method sample preparation. Arai and Tominaga observed that for a pressed Rh/Al₂O₃ disk (unspecified weight percentage of Rh) reduced at 673 K and exposed to 50 Torr CO at 298 K, followed by evacuation and exposure to O₂ at 50 Torr, the species II and III bands disappeared rapidly leaving only

the gem dicarbonyl species I bands [22]. Upon heating, the species I bands finally disappeared at 573 K. It is well-known that the order of disappearance of the surface species for supported Rh catalysts under evacuation in the absence of O_2 and under heating is $I > II > III$ [9-12,22] even though the order is $III > II$ for Rh single crystals [21] (no I can be present on metallic Rh). It has been observed in these laboratories also that following high temperature reduction (673 K) of a 10% Rh/ Al_2O_3 film and exposure to CO followed by evacuation, the species I infrared bands dominate upon exposure to O_2 at 298 K or at 673 K [10]. Kiss and Gonzalez [23] have shown recently that upon exposure of a 3% Rh/ SiO_2 pressed disk, reduced at 650 K, to a flowing stream of a CO/ O_2 mixture and upon heating to reaction ignition conditions, that the order of disappearance was $II, III > I$. They concluded that the oxidation rate of CO decreases in the sequence $Rh(0) > Rh(+1) > Rh(+1 \rightarrow +3)$ and that a new infrared band at 2104 cm^{-1} may be assigned to a CO/Rh surface species in which Rh is oxidized to at least +1 and possibly as high as +3.

Figures 1-3 show the results of heating prereduced 10% Rh/X ($X=Al_2O_3$, TiO_2 , and SiO_2) films to various temperatures in the presence of CO: O_2 mixtures (2:1). For all three samples CO_2 formation was first observed (by infrared) at ca. 380 K, and the intensities of all CO bands decreased at higher temperatures. In the case of 10% Rh/ Al_2O_3 (Fig. 1) the order of disappearance of the surface CO species was clearly $III > I > II$, and a small band at 2130 cm^{-1} in the 410 K spectrum can be assigned to CO bonded to Rh(+3) [10]. Thus we find that for a 10% Rh/ Al_2O_3 film exposed to a mixture of CO_2 and O_2 , that the linear species II is longest lived upon raising the temperature. A 0.5% Rh/ Al_2O_3 sample under the same

reaction conditions gave infrared spectra (not shown) with only species I bands present, as expected for the highly dispersed catalyst. The CO₂ band near 2340 cm⁻¹ had comparable intensity to that for the 10% Rh catalyst at a given temperature; this demonstrates that the gem dicarbonyl species as well as species II and III can be oxidized to CO₂. However, it should be noted that a substantial amount of CO₂ is produced over all of the support materials (Al₂O₃, SiO₂, and TiO₂) in the absence of Rh beginning at ca. 460 K. The infrared spectra of the blank supports do not contain any bands in the 1800-2100 cm⁻¹ region which could be attributed to adsorbed CO.

The infrared spectra of the 10% Rh/SiO₂ sample are shown in Fig. 2; unfortunately these spectra are complicated by the presence of background SiO₂ bands in the 2000 cm⁻¹ region making the observation of the bridged carbonyl (III) band behavior difficult. Nevertheless, employing difference spectra, we believe that the order of disappearance of the surface species upon increasing temperature for Rh/SiO₂ in this study was I>III>II. We could not detect any bands above 2100 cm⁻¹ characteristic of Rh in a higher oxidation state than +1. Clearly the linear CO surface species is dominant at temperatures above 380 K. For a 0.5% Rh/SiO₂ film the gem dicarbonyl species I bands were considerably less intense than was the case for 0.5% Rh/Al₂O₃. Furthermore, difference spectra show a very weak species II (linear CO) band which disappears last upon heating. This represents the first detection in these laboratories of a linear CO surface state on a 0.5% Rh catalyst film and probably is indicative of the greater ease of reduction of Rh on SiO₂ as compared to Al₂O₃ [12]. It possibly also indicates that some Rh cluster sites are present on 0.5%

Rh/SiO₂.

The infrared spectra of the 10% Rh/TiO₂ film (Fig. 3) show that the order of disappearance of the surface species upon heating was I>III>II as was the case for 10% Rh/SiO₂. It has been observed here [10-12] that 0.5% Rh/X films give symmetric and antisymmetric stretching mode bands for the gem dicarbonyl species I with roughly equal integrated intensities. However, for 10% Rh/X films the component near 2030 cm⁻¹ always exhibits higher integrated intensity. This is in part due to overlap with the species II band, but it also indicates the presence of another surface state [10]. This is demonstrated conclusively in Fig. 4 which shows infrared spectra for a 0.5% Rh/TiO₂ film exposed to the mixture of CO/O₂. Note that a new band is clearly resolved at 2000 cm⁻¹. Solymosi and coworkers have mentioned a shoulder near 2000 cm⁻¹ for a 0.3% Rh/TiO₂ disk exposed to CO[24]. They assigned this shoulder to a CO surface state on the TiO₂ support[24]. However, we saw no evidence for such a band for our blank TiO₂ film. Thus the presence of Rh is obviously necessary for the existence of this state. The frequency (2000 cm⁻¹) is too high to correspond to a bridged carbonyl on a Rh⁰ cluster. We believe that the state represents a bridged carbonyl between an isolated Rh⁺¹ ion and the support. This is consistent with the observation of higher CO stretching mode frequencies for oxidized Rh (Rh⁺¹ in species I, 2030/2100 cm⁻¹; Rh⁺², 2120 cm⁻¹; Rh⁺³, 2136 cm⁻¹) [10]. The 2000 cm⁻¹ band was not resolved in the spectra for 0.5% Rh/Al₂O₃ or 0.5% Rh/SiO₂, but we can not completely rule out its presence as a low frequency shoulder on the 2030 cm⁻¹ species I band component. It should also be noted that the 2100 cm⁻¹ component for 0.5% Rh/TiO₂ was abnormally intense (Fig. 4). This could indicate the

presence of a third surface state on this film. We have observed a similar effect near 2100 cm^{-1} for a 10% Rh/Al₂O₃ sample oxidized at 673 K before exposure to CO at 298 K [10]. We believe that this new state near 2100 cm^{-1} represents a single linear CO on Rh⁺¹ [10], or possibly to CO on a higher oxidation state of Rh as alluded to by Gonzalez and coworkers [23] for their Rh/SiO₂ disk.

4. Conclusions

We are not certain why our results differ from those reported in other laboratories [22,23], or even our own for a different type of experiment (exposure to CO followed by evacuation and subsequent oxidation), as regards the stability of the linear CO species II in a heated CO/O₂ mixture. We can only surmise that our sample-preparation procedures were substantially different in this study. Our low-temperature reduction probably led to a catalyst film dominated by Rh⁺¹. It is even possible that the stable linear CO state which we have observed really refers to a Rh⁺¹ monocarbonyl species.

Finally, we have observed for the first time a well-resolved band near 2000 cm^{-1} for CO/Rh/TiO₂ which has been assigned to a bridged carbonyl species involving an isolated Rh⁺¹ ion and the TiO₂ support.

Acknowledgement

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Figure Captions

Fig. 1 Infrared spectra of a 10% Rh/Al₂O₃ film (3.9 mg cm⁻²) as a function of temperature in the presence of 14.0 Torr CO/7.0 Torr O₂: (a) 300 K; (b) 30 min at 320 K; (c) 30 min at 350 K, then 30 min at 380 K; (d) 30 min at 410 K; (e) 30 min at 430 K; (f) 30 min at 450 K.

Fig. 2. Infrared spectra of a 10% Rh/SiO₂ film (4.7 mg cm⁻²) as a function of temperature in the presence of 14.0 Torr CO/7.0 Torr O₂: (a) 300 K; (b) 30 min at 320 K; (c) 30 min at 360 K; (d) 30 min at 380 K; (e) 30 min at 410 K, then 30 min at 430 K.

Fig. 3. Infrared spectra of 10% Rh/TiO₂ film (4.7 mg cm⁻²) as a function of temperature in the presence of 14.0 Torr CO/7.0 Torr O₂: (a) 300 K; (b) 30 min at 320 K; (c) 30 min at 350 K; (d) 30 min at 380 K; (e) 30 min at 410 K; (f) 30 min at 430 K.

Fig. 4. Infrared spectra of a 0.5% Rh/TiO₂ film (4.7 mg cm⁻²) as a function of temperature in the presence of 14.0 Torr CO/7.0 Torr O₂: (a) 300 K; (b) 30 min at 320 K; (c) 30 min at 380 K; (d) 30 min at 410 K; (e) 30 min at 430 K; (f) 30 min at 450 K.

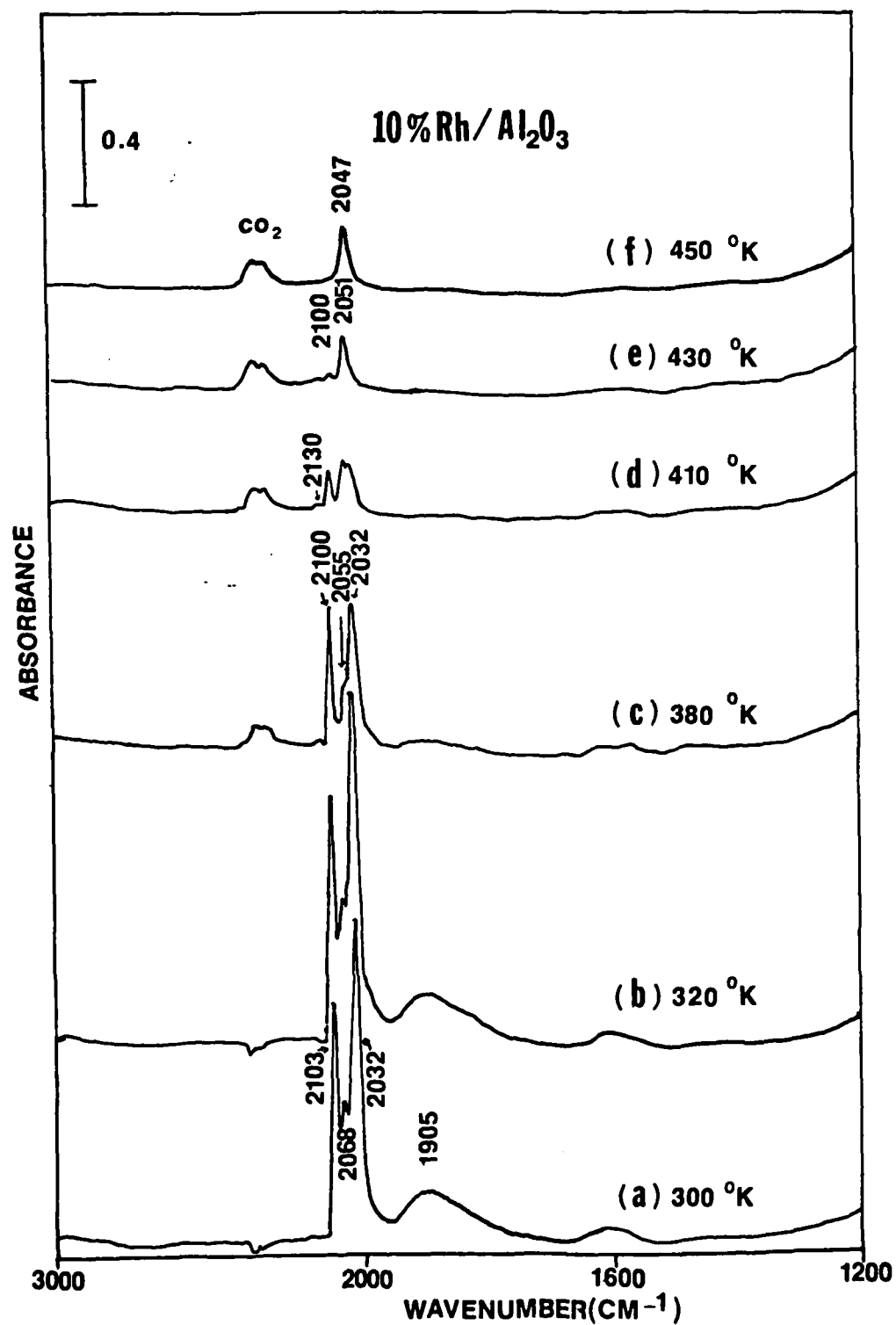


Fig. 1

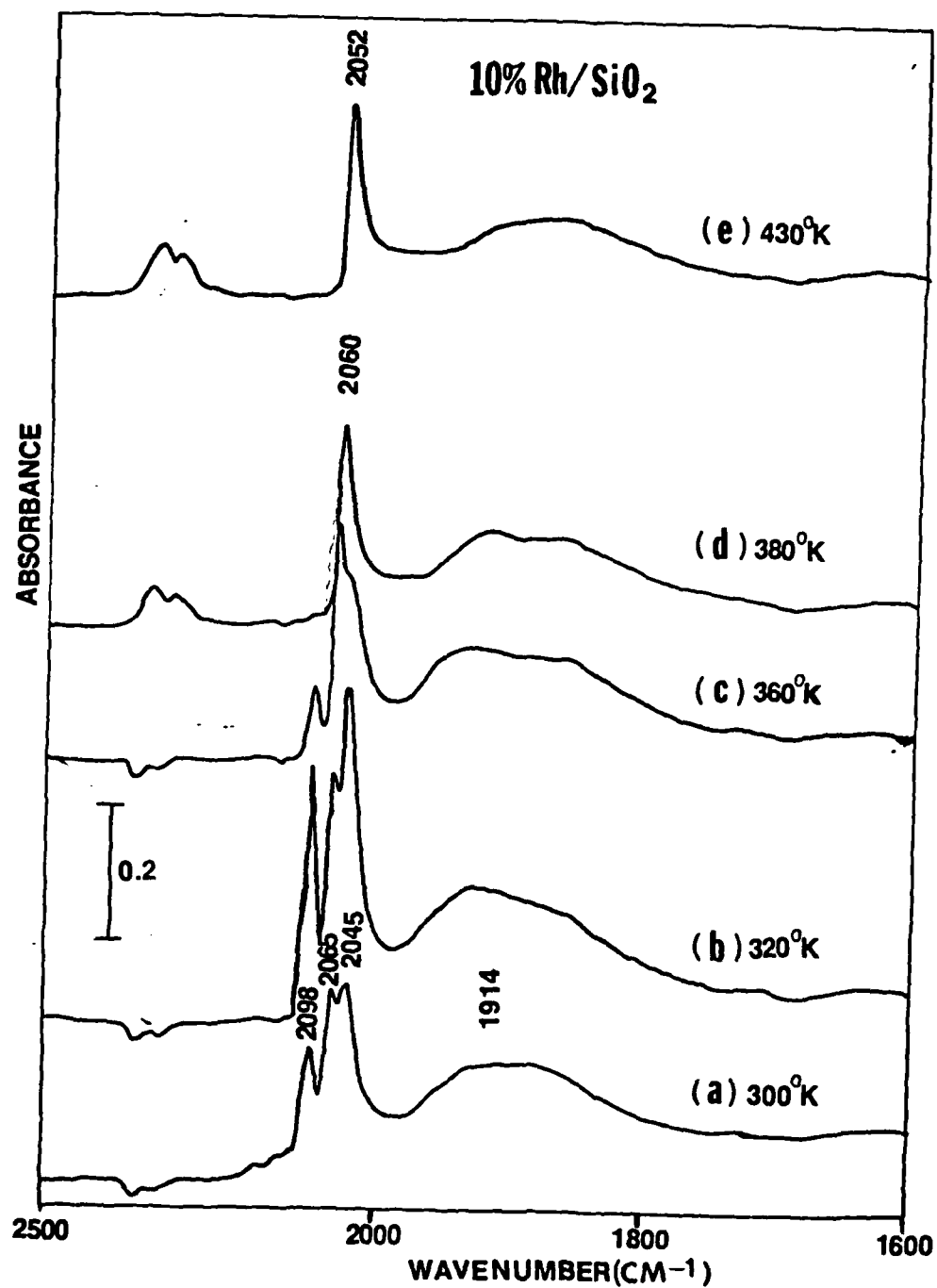


Fig. 2

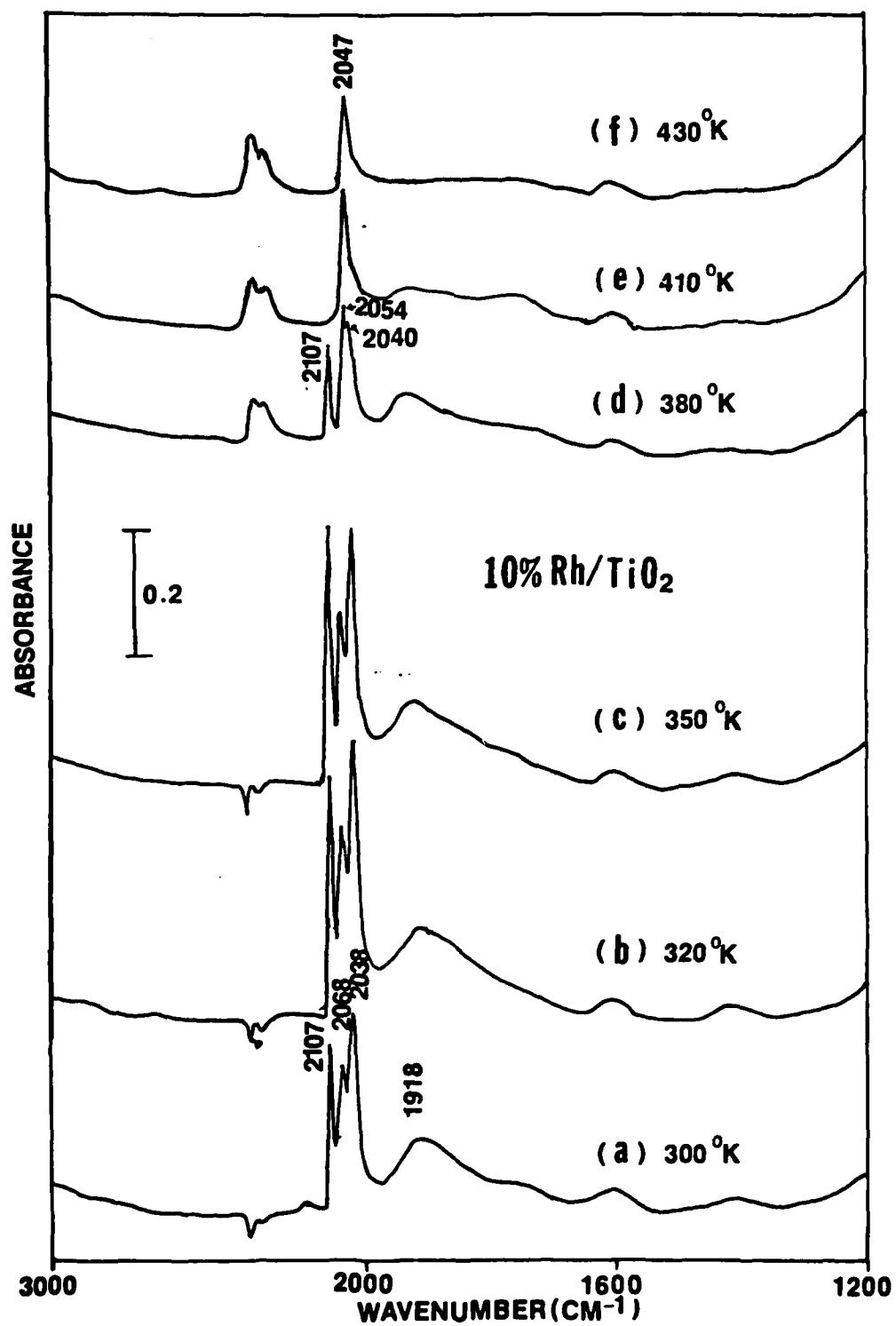


Fig. 3

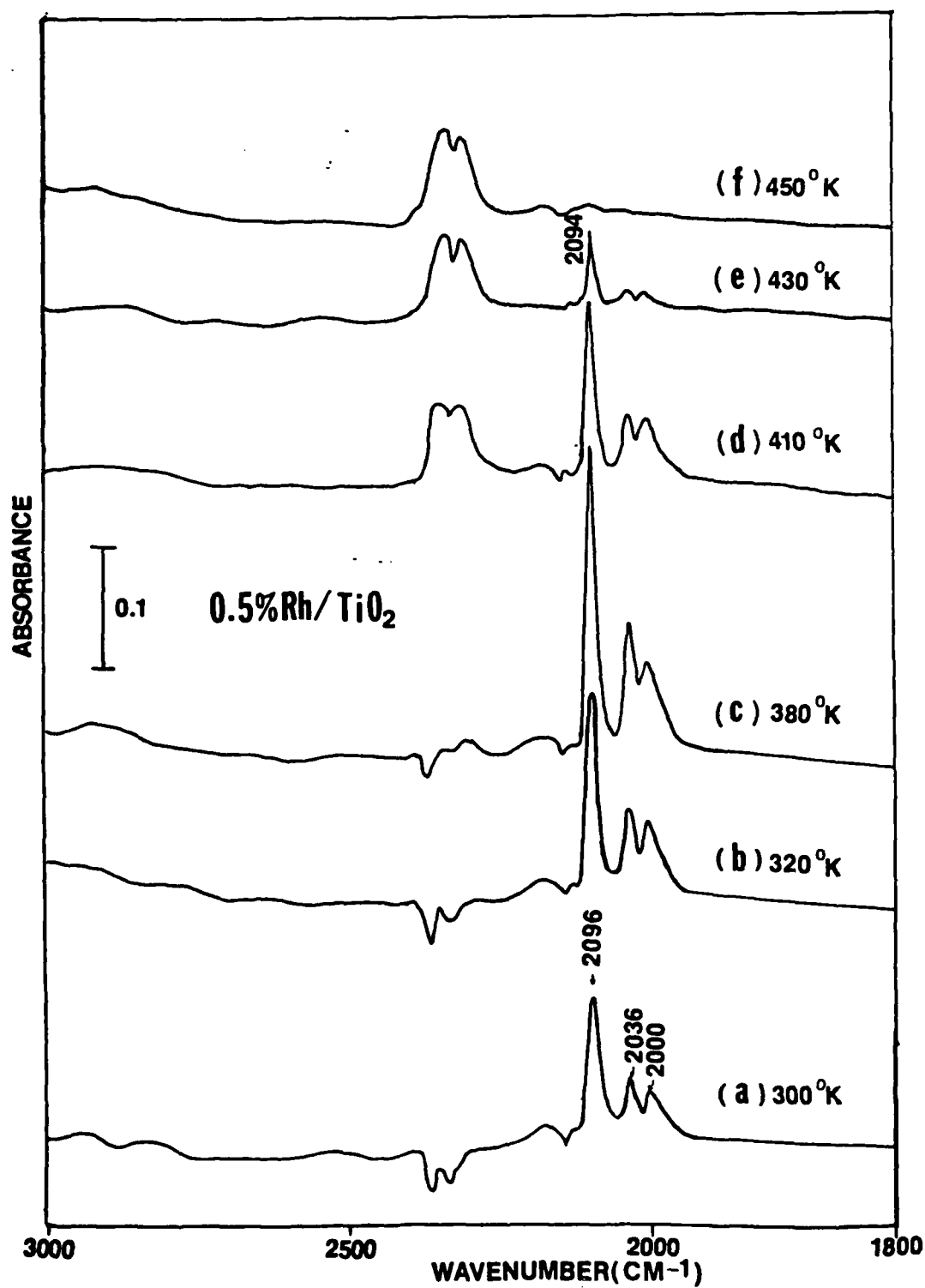


Fig. 4

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